Journal of Chromatography, 259 (1983) 350–352
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,582

Note

Gas chromatographic separation of mono-, di- and trimethyltin chlorides and tetramethyltin

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(Received November 30th, 1982)

Organotin compounds have found increasing use as pesticides, stabilers and catalysts during the last decade. The toxicity of several of these compounds has generated much interest in research. A recent issue of *Neurobehavioural Toxicology and Teratology* has been devoted exclusively to toxicological studies of trimethyltin and other organotin compounds[1]. Braman and Tompkins[2] and Hodge *et al.*[3] demonstrated the presence of non-volatile methyltin species in natural waters including both marine and freshwater sources. Several methods have been reported to separate and detect methyltin species. In one of these techniques, the compounds were converted to volatile hydrides that were separated by their boiling points[2–4]. In another method, the methylated tin species were first extracted with benzene using tropolone as the complexing agent, then butylated and finally separated by gas chromatography (GC)[5]. Methyltin halides could also be separated directly by high-performance liquid chromatography and GC[6]. In all these cases, the organotin compounds were measured by determining their tin content using atomic absorption or emission spectrometry. However, Burns *et al.*[6] reported that mono- and dimethyltin chlorides could not be separated by GC. They also observed on-column rearrangement of the methyltin species present in a mixture, and found that monomethyltin trichloride or tetramethyltin should be absent in order to avoid redistribution.

The present study describes a two-step procedure to separate and determine the four methyltin species (mono-, di-, trimethyltin chlorides and tetramethyltin) in a mixture by GC using a flame ionization detector.

EXPERIMENTAL

Reagents

Mono-, di- and trimethyltin chlorides and tetramethyltin were obtained from Alfa Chemicals. Appropriate concentrations of these compounds were prepared in dichloromethane singly or in a mixture.

Gas chromatography

The instrument was a Bendix Model 2500 gas chromatograph equipped with a flame ionization detector. A glass column (2 m × 4 mm) packed with 5% OV-101

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0021-9673/83/0000–0000/$03.00

on Chromosorb W HP (100–120 mesh) was used with oven, inlet and detector temperatures set at 52, 130 and 150°C respectively. A second glass column (2 m × 2 mm) packed with 5% OV-17 on Chromosorb W HP (100–120 mesh) was used with oven, inlet and detector temperatures of 55, 150 and 190°C respectively. Nitrogen was used as the carrier gas at a flow-rate of 30 ml/min for both columns. The 5% OV-17 column was extensively silanized by repeated 5-μl injections of a solution of 10% trimethylchlorosilane in diethyl ether at 10-min intervals and increasing the column temperature for each injection by 30°C from 50°C up to 200°C. This was routinely done at the end of the day and the column was left overnight to condition at 200°C.

RESULTS AND DISCUSSION

It was not possible to separate all four tin compounds on one particular column. Either the tetramethyltin (b.p. 78°C) could not be separated from the solvent

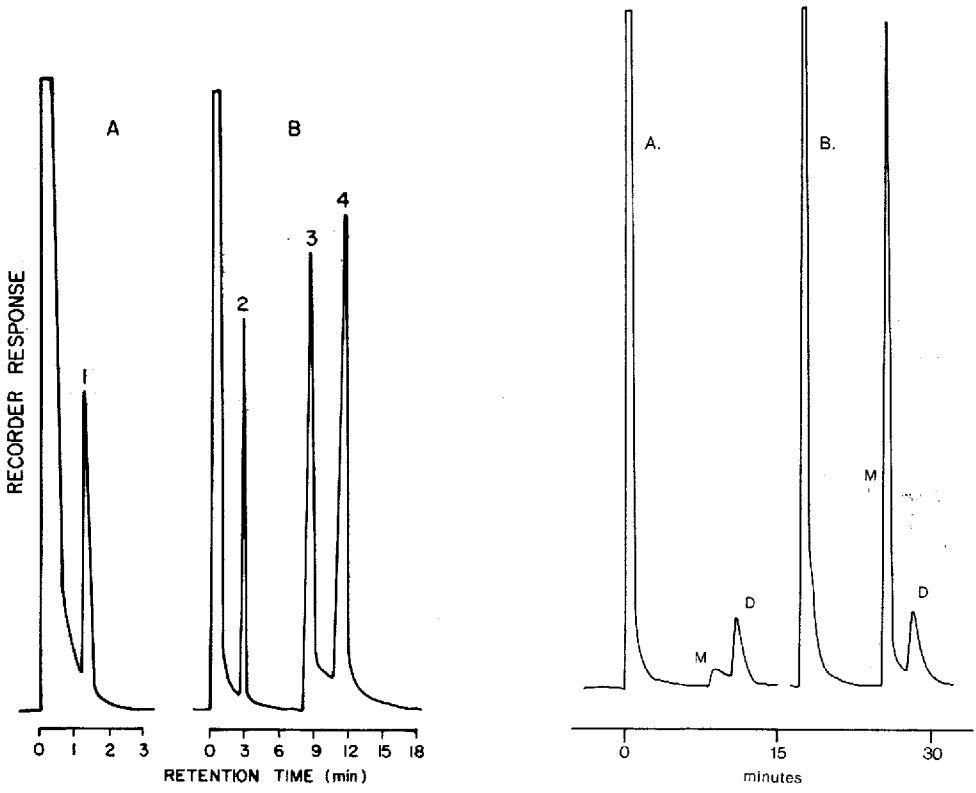

Fig. 1. Chromatograms of methyltin compounds: A, 5% OV-101 on Chromosorb W HP (80–100 mesh), 2.0 m × 4 mm I.D., sensitivity × 100; B, 5% OV-17 on Chromosorb W HP (100–120 mesh), 2.0 m × 2 mm I.D., sensitivity × 500. Peaks: 1 = $(CH_3)_4Sn$, 1 μg; 2 = $(CH_3)_3SnCl$, 1 μg; 3 = $(CH_3)SnCl_3$, 10 μg; 4 = $(CH_3)_2SnCl_2$, 12 μg.

Fig. 2. Chromatograms (on 5% OV-17) of monomethyltin trichloride (M) and dimethyltin dichloride (D) at weight ratios (M/D) of 0.5 (chromatogram A) and 8.0 (chromatogram B). Quantity of D injected: 1.0 μg.

using a polar stationary phase or incomplete separation of mono- and dimethyltin-chlorides was obtained using the non-polar stationary phase under isothermal or temperature programming conditions. However, the best results were obtained by using a column packed with 5% OV-101 on Chromosorb W HP (80–100 mesh) for tetramethyltin which was separated from the solvent (dichloromethane) as shown in Fig. 1A. Trimethyltin chloride was eluted after 10 min as a broad band. Mono- and dimethyltin chlorides were eluted after 20 min but no separation of these was obtained due to the excess tailing of monomethyltin trichloride. Because of this, another column (5% OV-17 on Chromosorb W HP, 100–120 mesh) was used to separate the mono-, di- and triméthyltin chlorides (Fig. 1B). Tetramethyltin was not detected because it coeluted with the solvent. Slight tailing of monomethyltin trichloride was still encountered, even though the column was extensively silanized and conditioned. Nevertheless, as shown in Fig. 2, the response (peak height) for dimethyltin dichloride, coinjected with monomethyltin chloride remained unchanged when the weight ratio of these two compounds was varied from 0.5 to 8.0 (mono:di). Moreover, no rearrangement reactions and decomposition were observed when the four methyltin species were present together since identical responses were obtained when they were analysed individually or in a mixture. This is in contrast to results reported by Burns *et al.*[6] and Arakawa *et al.*[7]. Our success in separation of these compounds may be due to the lower oven and inlet temperatures and the extensive silanization of the column. The detection limits (2 × background noise) were about 10^{-8} g for tetramethyltin and trimethyltin chloride, and 10^{-7} g for di- and monomethyltin chlorides. The relative standard deviations for six replicate injections were less than 5% for all compounds at concentrations five-fold above the detection limits. Linear response was obtained for solution concentrations up to the mg/ml range.

In conclusion, the present study demonstrates a two-step GC procedure to determine directly the four methyltin species in a mixture using a commonly available flame ionization detector.

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